THE EFFECT OF INITIAL NO_x LEVELS ON SELECTIVE NON-CATALYTIC NO_x REDUCTION PERFORMANCE

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ABSTRACT

The primary parameters affecting NO_x reduction performance of SNCR processes include injection temperature and the chemical N/NO_x molar ratio. Previous work showed that SNCR performance was also dependent upon initial NO_x levels. This is of concern for future applications to oil- and gas-fired systems, where initial NO_x levels of 30 to 100 ppm may be anticipated after combustion modifications are implemented.

To quantify the effect of these low initial NO_x (NO_i) levels on SNCR performance, a pilot-scale test program was performed to investigate the effect of NO_x levels with both urea and ammonia injection. This pilot test program evaluated the effect of NO_x levels ranging from 30 to 200 ppm on process performance. A range of temperature and N/NO_x ratios was evaluated for each SNCR chemical. The laboratory effort was supported by chemical kinetic modeling of the SNCR process. Test results included characterization of both the ammonia and urea injection processes. The effect of process parameters on NO_x reduction, and secondary emissions including NH_3, N_2O, and CO emissions was characterized. The laboratory data revealed important information regarding the implementation of SNCR processes at low initial NO_x levels.

INTRODUCTION

Since NO_x plays a major role in the formation of photochemical smog (Ref. 1), regulations requiring NO_x emissions reductions have been enacted in many areas. For example, NO_x emissions from utility boilers in the South Coast Air Quality Management District have been reduced significantly from their baseline, uncontrolled levels through the implementation of combustion modification techniques.

To meet upcoming regulations, which mandate further NO_x emission reductions, alternate control methods may be required. One approach under consideration involves the use of selective non-catalytic NO_x reduction (SNCR) techniques in conjunction with advanced combustion modification techniques. Both urea and ammonia injection have been shown to provide NO_x reductions at full-scale for a variety of combustion devices.

The primary parameters affecting NO_x reduction performance of SNCR processes are the injection temperature and N/NO_x molar ratios. Previous work (Ref. 2) also showed the dependence of process performance on initial NO_x levels. This is a concern for future applications to oil- and gas-fired systems, where initial NO_x levels of 30 to 100 ppm may be anticipated after combustion modifications are implemented.

In order to quantify the effect of these low initial NO_x (NO_i) levels on SNCR performance, a test program investigating the effect of NO_i levels with both ammonia and urea injection was performed. This laboratory test program evaluated the effect of NO_i levels ranging from 30 to 200 ppm on process performance for both urea and ammonia injection. Urea injection tests were performed over a temperature range of 1600 to 2075°F at varying reagent injection rates. Ammonia slip was measured, using wet chemical techniques at selected urea injection conditions. Ammonia injection tests were performed over a temperature range of 1470 to 1900°F. The laboratory experimental effort was supported by chemical kinetic modeling of the urea injection process using CHEMKIN.

FACILITY DESCRIPTION

The tests were performed using a natural gas-fired pilot-scale combustor facility. This facility has a design heat input of 300,000 Btu/hr, and a combustion product flowrate of 47 SCFM. This provides a nominal residence time of 0.5 second in the test section at 1800°F. Combustion gas temperatures entering the test section are controlled by adjusting the firing rate and with a series of adjustable water-cooled probes. Heat removal is controlled by varying the number and insertion depth of individual probes. The unit has a temperature gradient of 400-500°F/second over the test section length. While this is relatively high compared to other laboratory facilities, it was designed to match the temperature gradients typical of utility boiler environments.

Liquid and/or gaseous reagents were injected into the combustion products using water-cooled injectors. Gaseous NH_3 was injected using diametrically opposed injectors. The liquid urea solution was injected using a single small water-cooled atomizer.

A suction pyrometer was used to measure true gas temperatures at the entrance to the test section. For this test program, all gas analysis sampling was performed at the test section exit. A portion of the sample was taken from the sample probe exit and transported to the gas analysis instrumentation by a heated Teflon sample line. Before passing through the analyzers, the sample was dried in a refrigerated dryer. The dried sample was analyzed for NO, NO_x, O_2, CO, CO_2, N_2O and O_2, using continuous electronic gas analyzers. Ammonia concentrations were determined by passing a gas stream through an impinger train containing a dilute sulfuric acid solution. The ammonia concentration was subsequently determined using a specific ion electrode.

NH_3 INJECTION TEST RESULTS

The ammonia injection tests were performed using initial NO_x levels ranging from 30 to 200 ppm. Injection temperatures ranged from nominally 1470 to 1900°F. The N/NO_x ratio, the molar ratio of nitrogen in the SNCR chemical to the inlet NO_x, characterizes the amount of chemical injected. N/NO_x molar ratios of 1.0 and 2.0 were evaluated during these tests.

Figure 1 shows NO_x reduction data plotted versus temperature for tests performed at N/NO_x ratios of 1.0 and 2.0, and varying initial NO_x levels. A number of observations can be made from the data in Figure 1. First, the level of NO_x reduction decreases as the initial NO_x level decreases. Also, the optimum injection temperature appears to shift to higher temperatures as the initial NO_x level increases. Conversely, operation at low initial NO_x levels appears to require injection at reduced temperatures to obtain optimum results. This trend was observed for tests performed at both N/NO_x molar ratios. This temperature shift increases as the N/NO_x ratio increases. A final observation can be made about the effect of initial NO_x level at low injection temperatures. Over the majority of the temperature range, decreasing the initial NO_x level decreased NO_x reduction. However, as can be seen in Figure 1, at temperatures below nominally 1500°F, decreasing the initial NO_x level results in an increase in NO_x removal (albeit the overall levels of NO_x reduction are small).

UREA INJECTION TEST RESULTS

The urea injection tests were conducted using an aqueous urea solution. Solution flow rates were held constant for these tests to maintain a constant thermal environment in the injection zone. To change the N/NO_x ratios, the concentration of the urea solution was varied.

For the urea injection tests, gaseous emissions measurements were made over a temperature range of 1600 to 2075°F. Initial NO_x levels were varied from 30 to 200 ppm, while molar ratios of N/NO_x were varied from 0.5 to 4.0. Byproduct ammonia emission measurements, performed in conjunction with urea injection, were made over a more limited matrix. A temperature range of 1600 to 1940°F was used for performance of the subsequent byproduct NH_3 emissions (NH_3 slip) tests. NH_3 measurements were not made at temperatures in excess of 2000°F, since previous tests have shown that ammonia emissions are negligible at these high temperatures. Molar N/NO_x ratios of 0.5, 1.0 and 2.0 were evaluated during these tests for initial NO_x levels of 30, 70 and 200 ppm (in the present paper, only the results obtained for a N/NO_x molar ratio of 2.0 are shown).

Figure 2 shows NO_x reduction as a function of injection temperature for urea injection tests performed at a N/NO_x molar ratio of 2.0. The results are similar to the ammonia test results shown in Figure 1. These data also show that NO_x reductions decreased with decreasing initial NO_x levels. This trend was evident for all injection temperatures. It was also evident that the optimum injection temperature decreased as initial NO_x levels decreased. Also note that at low temperatures (i.e., less than 1600°F), decreasing the initial NO_x level increased NO_x reduction.

Ammonia slip data are plotted in Figure 3, which shows NH_3 concentration versus temperature as a function of initial NO_x level at a N/NO_x molar ratio of 2.0. As expected, the data show that NH_3 emissions increase with initial NO_x level and decrease with temperature.

N_2O has been found to be a product of the reaction between urea and NO_x. N_2O production is plotted as a function of temperature for operation at a N/NO_x molar ratio of 2.0 in Figure 4. The data show that, below 2010°F, N_2O emissions increased with increasing temperature, regardless of initial NO_x level or N/NO_x ratio. At temperatures above 2010°F, the N_2O emissions decreased. N_2O emissions also increased with both the N/NO_x and initial NO_x levels, as expected. Comparison with data reported previously show that N_2O production peaks at approximately the same temperature as NO_x reduction.

The slope of the N_2O versus temperature curves increased as initial NO_x levels increased for all of the N/NO_x ratios. This change in sensitivity likely reflects the quantity of reagent available to react at the differing injection rates.

CHEMICAL KINETICS MODELING RESULTS

In support of the laboratory urea injection tests, a series of chemical kinetic calculations were performed to investigate the effect of initial NO_x level upon the urea temperature and NO_x reduction, in particular, the behavior of the initial NO_x level at low temperatures. The chemical kinetics calculations were performed over a temperature range of 1472 to 1992°F at initial NO_x levels of 30, 70 and 200 ppm. Urea injection rates were set to give a N/NO_x molar ratio of 2.0. Combustion products were set at a stoichiometry comparable to the pilot-scale work. The urea was assumed to decompose as NH_3 and HNCO.

The chemical kinetics calculations were performed using a PC version of SANDIA's CHEMKIN program. The mechanism used was that of Miller and Bowman (Ref. 3). A residence time of 2.0 seconds was used in the calculations.

Calculated NO_x reductions, NH_3 slip and N_2O production for a N/NO_x ratio of 2.0 are plotted as a function of temperature at three initial NO_x levels (30, 70, and 200 ppm) in Figure 5. For an initial NO_x level of 200 ppm, the calculated chemical kinetics data show that a peak NO_x removal of approximately 100 percent occurred at 1740°F. At an initial NO_x level of 70 ppm, the maximum NO_x removal decreased to approximately 90 percent and occurred at a temperature of 1605°F. When the initial NO_x was decreased to 30 ppm, the maximum NO_x removal decreased to 80 percent and occurred at approximately 1520°F. The calculations indicate that decreasing the initial NO_x concentration shifts the temperature window and reduces the maximum achievable NO_x reduction. In spite of the shift in optimum temperature and maximum reduction, the shape of the window appears to remain essentially the same over the range of conditions evaluated. At low temperatures, the calculated results also show an increase in NO_x reduction with decreasing initial NO_x level (Figure 5).

The model predicts higher NO_x removals and slightly different temperature windows than were seen experimentally. However, the experimental results follow the same trends predicted by the model calculations. As initial NO_x levels decrease, the temperature window shifts to lower temperatures and the maximum amount of NO_x removal decreases.

The NH_3 slip and N_2O levels predicted by the model also support the experimental results (Figure 5). The model predicts the increase in NH_3 and N_2O with increasing NO_x levels, and their decrease with increasing injection temperatures. However, the model predicts lower levels of NH_3 and N_2O than observed experimentally; in addition, the model predicts N_2O production at temperatures lower than those observed experimentally. Part of these differences can be ascribed to the thermal profiles. The calculations were done assuming isothermal conditions while the experimental combustor exhibits a temperature gradient of 400-500°F/second.

CONCLUSIONS

Based on the data presented above, the following conclusions can be drawn for both urea and ammonia injection:

- Reducing initial NO_x levels results in 1) a decrease in NO_x reduction performance, and 2) a decrease in optimum injection temperatures.

The following conclusions can be drawn for urea injection:

- Decreasing temperatures result in increasing NH_3 emissions.
- Below 2010°F, increasing urea injection rates result in increasing N_2O emissions. However, N_2O emissions decrease at temperatures above 2010°F.

Chemical kinetic modeling of the urea injection process showed trends similar to those seen during performance of the laboratory tests.

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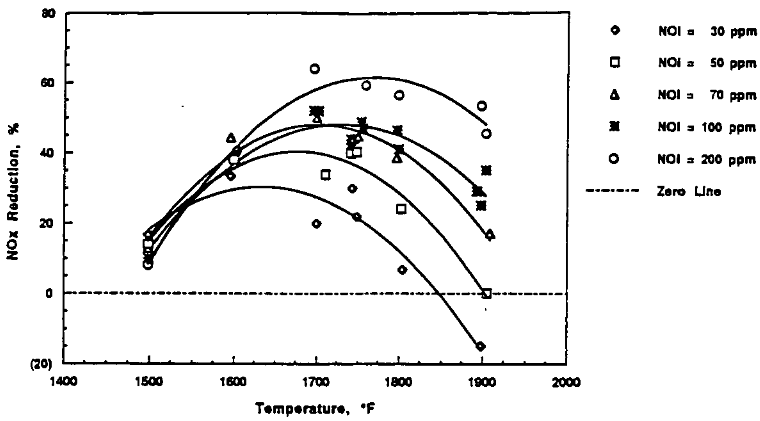
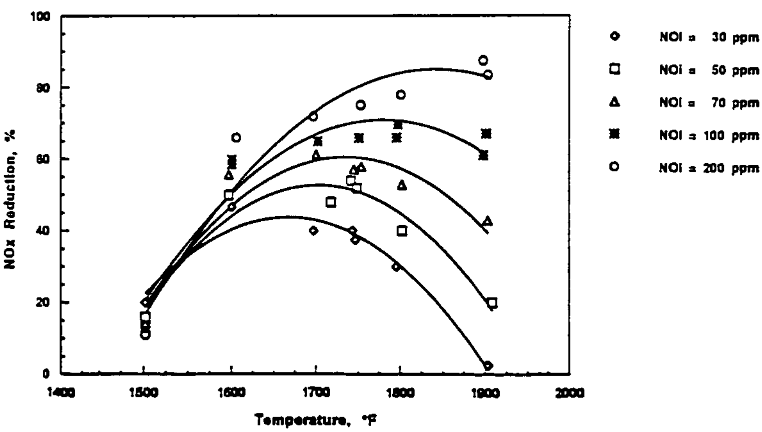


(a) $N/NO_x = 1.0$



(b) $N/NO_x = 2.0$

Figure 1. Laboratory test results with NH_3 injection. Effect of injection temperature on NO_x removal at variable initial NO_x levels

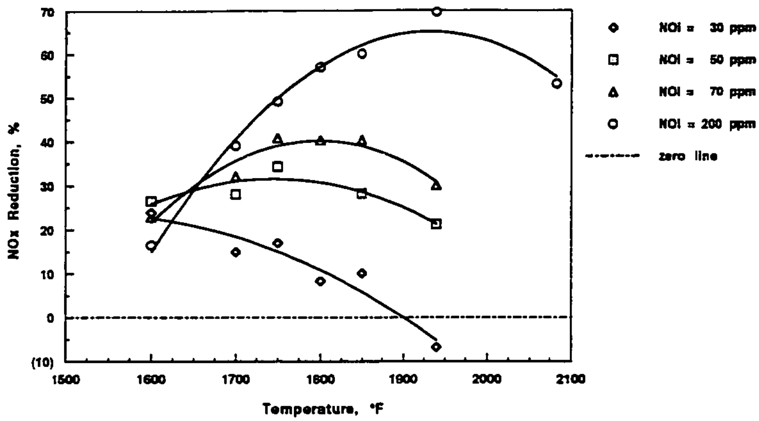


Figure 2. Laboratory test results with urea injection. Effect of injection temperature on NO_x removal at variable initial NO_x levels

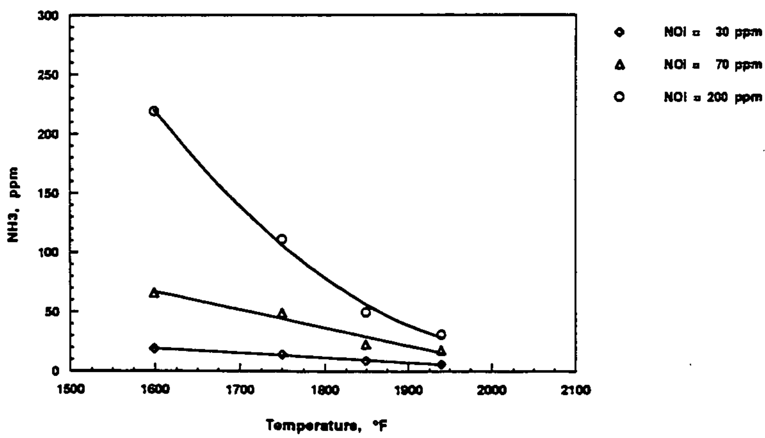


Figure 3. Laboratory test results with urea injection. Effect of injection temperature on NH_3 emissions at variable initial NO_x levels, $N/NO_x = 2.0$.

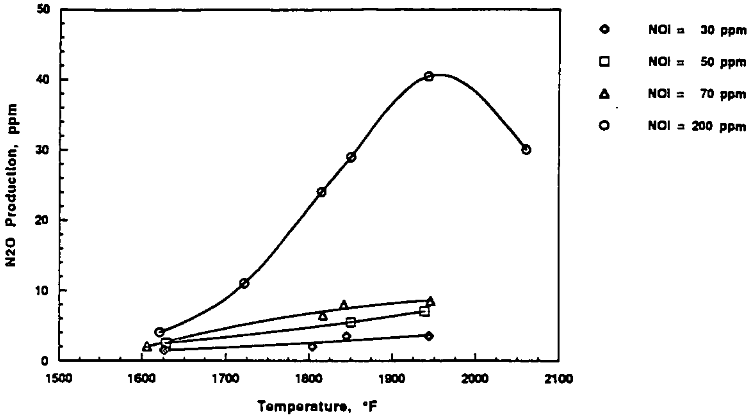
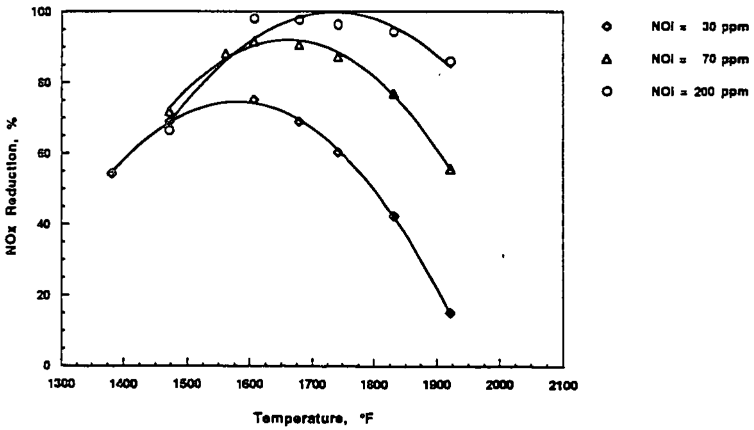
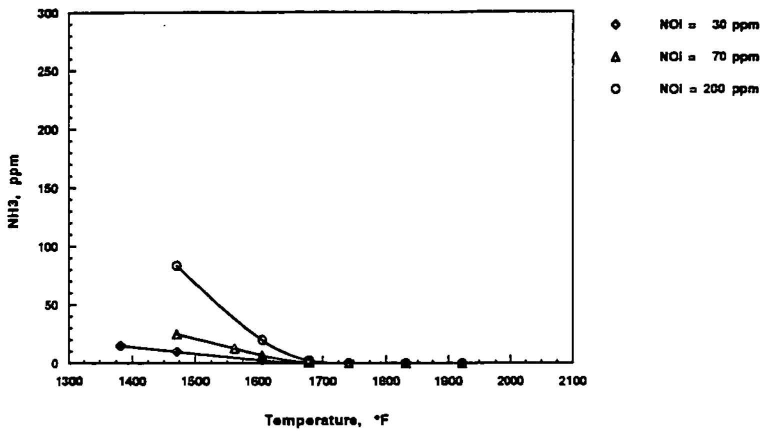


Figure 4. Laboratory test results with urea injection. Effect of injection temperature on N_2O emissions at variable initial NO_x levels, N/NO_x = 2.0.

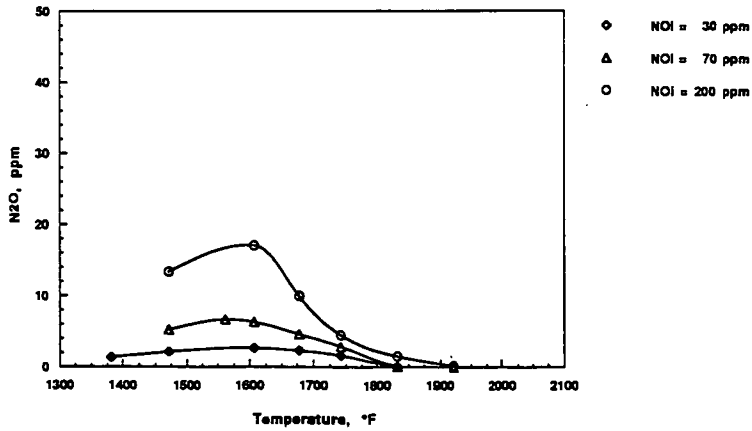


(a) NO_x Reduction

Figure 5. CHEMKIN chemical kinetics modeling results showing the predicted effect of temperature on NO_x reduction with urea injection.



(b) NH_3 Emissions



(c) N_2O Production

Figure 5. CHEMKIN chemical kinetics modeling results showing the predicted effect of temperature on NO_x reduction with urea injection.